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PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Lubricating Grease

We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, having an office at Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a lubricating grease suitable for lubrication of anti-friction bearings.

A general property of the normally solid greases of the invention is good ability to shear-harden when a shearing stress is exerted on the grease. This ability to shear-harden is of particular importance in the lubrication of anti-friction ball bearings. In such ball bearing lubrication, a non-hardening type grease tends to churn in the rotating bearing, thereby imparting resistance to the rotation of the bearing, which in turn increases friction and generates unwanted heat. On the other hand, when using the grease of this invention, the rotating bearing shear-hardens the grease. The result is that the rotating balls, or rollers, will after a time form a channel through the grease. Once the channel is formed, the grease is still available for lubrication, but does not impede the rotating balls or bearing movement, thereby giving lower torque requirements, less friction, a lower power requirement and a cool-running bearing.

Channelling-type grease, are of course known, and are preferred for lubrication of anti-friction bearings for lubricated-for-life electric motors, since the bearings do not require as much torque to turn as those lubricated with a non-channelling grease. However, in a new motor, prior channelling-type greases frequently cause loud whistling and other bearing noises. These noises usually abate after the motor is used for a time and becomes broken-in. However, these initial noises are very undesirable because of their unfavourable effect on the consumer, who might thereby think the motor is defective. On the other hand, a non-channelling type grease, by churning in an operating bearing, dampens this bearing noise (which is usually caused by separator-flutter) although the non-channelling grease is much less satisfactory for lubricating the motor. Now a very important aspect of the present invention is the formation of a grease which allows short-term initial churning of the grease in bearings to thereby prevent noise, but which gradually becomes a channelling grease during use.

Accordingly the present invention provides a lubricating grease composition comprising a major amount of lubricating oil and a minor amount of a mixed salt combination of alkali metal salts of a) C_2 — C_4 fatty acid, b) C_6 to C_{10} aliphatic dicarboxylic acid or alkyl polynuclear aryl dicarboxylic acid and c) C_{12} to C_{24} fatty acid, in a molar hydrogen equivalent ratio of 1 to 10 molar hydrogen equivalent proportions of the C_2 — C_4 fatty acid per molar hydrogen equivalent of the dicarboxylic acid, and 1 to 4 molar hydrogen equivalents of the C_{12} to C_{24} fatty acid per molar hydrogen equivalent of said dicarboxylic acid.

In contrast to previously known greases, the greases of the invention do not become excessively fluid at elevated temperatures, or become excessively rubbery or fibrous at elevated temperatures, due to phase changes in the soap-thickening structure.

The mixed-salt thickener systems of the invention are best made to contain alkali metal salt of 3 to 6 molar hydrogen equivalents of C_2 to C_4 fatty acid per molar hydrogen equivalent of C_6 to C_{16} dicarboxylic acid, and 1 to 3 molar hydrogen equivalents of C_{12} to C_{24} fatty acid per molar hydrogen equivalent of said dicarboxylic acid. Greases can be thus prepared having a total content of said salts of 5.0 to 49.0 weight percent, preferably 20 to 45 weight percent, based on the weight of the grease. These greases in turn can be diluted with additional oil to form fluid or semi-fluid compositions containing 0.1 to 5.0% of the mixed salt.

Suitable low molecular weight acids for forming the mixed salt compositions of the invention include fatty acids such as acetic and propionic acids. Acetic acid or its anhydride is preferred.

The C_{12} to C_{24} fatty acids or aliphatic carboxylic acids useful for forming the mixed salt of the invention include naturally-occurring or synthetic, substituted or unsubstituted, saturated or unsaturated, mixed or unmixed fatty acids, preferably those having 16 to 24 carbon atoms per molecule. Examples of such acids include myristic, palmitic, stearic, 12-hydroxy stearic, arachidic, oleic, ricinoleic, hydrogenated fish oil, and tallow acids.

Recently, a very low price fatty acid material comprising chiefly elaidic acid with minor amounts of oleic acid (9-octadeceneoic acid), and other isomers of oleic acid, e.g. 12-octadeceneoic acid and linoleic acid, etc. has become commercially available under the general name of iso-oleic acid. This acid primarily differs from pure oleic acid in that its chief component, i.e. elaidic acid, is in the cis or syn isomeric form, rather than in the more common trans or anti form of oleic acid.

The iso-oleic acid may be 100% oleic acid in the cis form, i.e. elaidic acid. However, commercial iso-oleic acid generally constitutes mixtures of a major amount of elaidic acid with minor amounts of oleic acid (i.e. 9-octadeceneoic acid) and other related acids such as 12-octadeceneoic, linoleic, stearic, and palmitic.

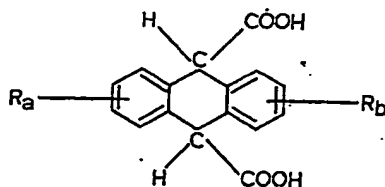
An iso-oleic acid, available from Emery Industries, under the name Emery 636 fatty acid, was used in the working examples of the invention. This acid had the following typical characteristics:

Titer*, °C.	32°C.
Iodine Value (Wijs)	70
Free Fatty acids (% as oleic)	91
Acid Value	182
Saponification Value**	189
Color, Gardner	8

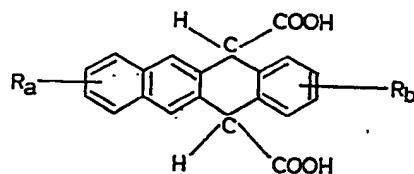
*The titer noted above is a false titer, since in derivatives, the acid acts as a lower titered acid.

**Contains an inter-ester easily broken by saponification techniques.

The dicarboxylic acid of the invention includes aliphatic acid of 9 to 16, preferably 10 to 12 carbon atoms, which can be either straight or branched chain. Examples of such acids include azelaic, sebacic and dodecanedioic acids. Higher aliphatic dicarboxylic acids appear to result in greases of shorter lubrication life at elevated temperatures and therefore are not preferred for this invention. Instead of said C_6 to C_{16} aliphatic dicarboxylic acid, certain polynuclear aromatic dicarboxylic acids can be used. These polynuclear acids can be typified by the formulas:



and



where R represents alkyl groups containing 1 to 8 carbon atoms, a and b can be 0 to 4, the sum of a and b being at least 1 but usually be no greater than 6. A particularly preferred aromatic polynuclear dicarboxylic acid is available from petroleum refining and can be formed by treatment of the highly aromatic extract derived by extraction of catalytic cracking cycle stock, with CO₂ and sodium to form a salt of the aromatic acid, said salt being subsequently hydrolyzed with strong acid to separate the free dicarboxylic acid. The exact nature of the resulting dicarboxylic acid is not known with certainty but analysis shows it to be mainly 3 and 4 ring alkyl polynuclear dicarboxylic acids of the two types shown by the formulas above.

The metal component of the mixed thickeners is an alkali metal, preferably sodium and/or lithium.

The lubricating oil used in the compositions of the invention may be either a mineral lubricating oil or a synthetic lubricating oil. Synthetic lubricating oils which may be used include esters of dibasic acids (e.g. di-2-ethylhexyl sebacate), esters of glycols (e.g. C₁₂ Oxo acid diester of tetraethylene glycol), complex esters (e.g. the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethyl-hexanoic acid), halohydrocarbon oils, alkyl silicates, sulfite esters, mercaptals, formals, polyglycol type synthetic oils, or mixtures of any of the above in any proportions. If the salts are formed in situ in the oil, then this *in situ* reaction is best carried out in a mineral oil, since many synthetic oils will tend to decompose or hydrolyze during the salt formation. However, the salts once formed, can be used in lubricants containing the synthetic oils noted above.

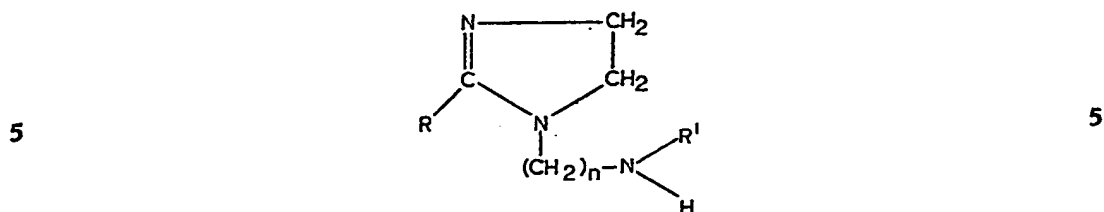
It has been further found that by the addition of alkali metal phosphates, e.g. trisodium ortho phosphate, to the grease, that not only does a harder grease result but the trisodium phosphate imparts anti-oxidation properties and increases the lubrication life of the grease. Usually, 0.1 to 6.0, preferably 1.0 to 6.0 wt. %, of trisodium phosphate will be used. On using amounts of trisodium phosphate in excess of the recited ranges, the grease structure will generally become undesirably rubbery and cohesive. The trisodium phosphate is preferably added in as finely divided form as possible to avoid imparting grittiness to the grease as can otherwise occur when the trisodium phosphate particles are too large.

Various other alkali metal salts of phosphoric acid can optionally be included in the greases of the invention, such as lithium ortho phosphate, potassium ortho phosphate, sodium pyrophosphate, and sodium tripolyphosphate. However, trisodium orthophosphate is preferred, since it is economical and, in general the most effective of these salts in imparting antioxidant, antiwear and some load-carrying ability to the grease.

The trisodium phosphate can be incorporated in the grease in a number of different ways. However, it should preferably be present in a finely divided form, e.g. 15 microns or less, in order to secure good stability and avoid grittiness of the grease. One method of obtaining such finely divided trisodium phosphate in the grease of the invention is to form it *in situ* in the oil by neutralizing ortho phosphoric acid, in the oil, with sodium hydroxide. Or, preformed trisodium phosphate mechanically milled to very fine particle size, can be simply dispersed in the grease. Or, preformed trisodium phosphate can be prepared *in situ* in a carrier by neutralizing phosphoric acid with sodium hydroxide, then precipitating the trisodium phosphate from said carrier in the presence of a protective material which will coat the small particles of trisodium phosphate as they precipitate. Still another method involves crystallizing trisodium phosphate from an aqueous solution in the presence of oil containing a protective stabilizing material. Trisodium phosphate prepared by this last-mentioned method, using an imidazoline salt as the stabilizing material, was used in the Examples of the invention. Specifically, in this last-mentioned method, trisodium phosphate is dissolved in water, preferably to form a saturated solution. This solution is then added to a small amount of mineral oil in which is dispersed a surface active agent of the amino imidazoline salt type. The resulting mixture is heated to drive off most of the water. The mass is then cooled to form a grease-like solid mass containing finely

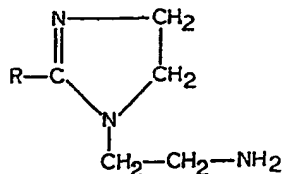
divided particles of dry trisodium phosphate coated with the amino imidazoline salt. This grease-like mass can then be used in preparing the grease of the invention.

The amino imidazolines useful to form the salt surfactant in the just-described process, include those having the general structure:



10 In the above formula, n is 2 to 6, preferably 2 to 3; R is a C₆ to C₂₂, preferably a C₁₆ to C₁₈, hydrocarbon group, either saturated or unsaturated, and preferably aliphatic; while R' is either hydrogen or a C₁ to C₁₈ alkyl group; preferably R' is hydrogen and n is a small integer, e.g. 2, in order that the effectiveness of the imidazoline is as great as possible per pound of material. In other words, the effectiveness of the imidazoline in the present invention apparently depends on the ring structure and the terminal amino group, while the number of carbon atoms in the branches merely dilute the effectiveness of the material per pound of imidazoline.

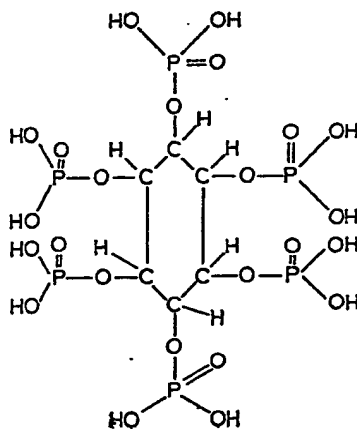
15 A specific example of imidazoline of the above formula, which was used in the working examples of the invention, was a commercial 1 - (2 amino ethyl - 2 - n - alkenyl - 2 - imidazoline) having the formula:



20 wherein R represents heptadecenyl and heptadecadienyl chains in a mol ratio of about 1:1, respectively. This product is available under the name Nalcamine G-39M.

The acid reacted with the imidazoline to form the salt surfactant, includes inorganic mineral acids such as ortho, pyro and meta phosphoric acids, hydrochloric acid, sulfuric acid, nitric acid, and also phytic acid which is closely related to phosphoric acid and possibly forms phosphoric acid salt in the present process.

25 Phytic acid is the hexaphosphosphoric acid ester of inositol. It is a strong acid containing twelve acidic hydrogen groups. Its structural formula is believed to be as follows:



This material, having a molecular weight of 660 with 12 reactive hydrogen groups, has a combining weight (mol equivalent weight) of 55.

Phytic acid is derived from grain, and is a by-product from waste corn steep liquor. A description of phytic acid and its preparation is given in Chemical Engineering, January 27, 1958, under the title "Ion Exchange Now Yields Phytic Acid", published by McGraw-Hill Publishing Co., Inc., New York, New York.

The amino imidazoline salt is prepared by mixing the imidazoline and appropriate acid, preferably in a small amount of inert hydrocarbon oil, to form the imidazoline salt. Then, an aqueous solution, preferably saturated, of the salt to be finely divided, e.g. trisodium phosphate, is stirred into the mixture of oil and the imidazoline salt. Then, water is removed by heating or distillation to form a grease-like mass, which can be then used in preparing the final grease composition.

If a stabilizer for the alkali metal phosphate is used, then usually 5 to 40, e.g. 10 to 30 wt. % of stabilizer, based on the weight of alkali metal phosphate, will be used.

Various other additives may also be added to the lubricating composition (e.g. 0.1 to 10.0 weight percent) of detergents such as calcium petroleum sulfonate; oxidation inhibitors such as phenyl-alpha-naphthylamine; corrosion inhibitors, such as sorbitan monooleate; dyes; and other grease thickeners.

The lubricants of the invention can be formed in a number of different ways. The most convenient is to conneutralize all the carboxylic acids in at least a portion of the oil, with alkali metal base. Usually, the resulting composition will then be heated to 300° to 550°F., preferably 400 to 500°F. to dehydrate the composition. The higher temperature of 400 to 500°F. will result in the formation of a salt material having greater thickening effect and better load and e.p. properties than the lower dehydration temperatures.

The invention is further illustrated by the following Examples:

EXAMPLE I

58.5 parts of mineral lubricating oil of 55 SUS viscosity at 210°F., 15 parts of isooleic acid (Emery 636 Fatty Acid) and 4 parts of sebacic acid were charged to a fire-heated grease kettle and intimately mixed. 10 parts of glacial acetic acid was then added to the kettle, followed immediately by the addition of 11.5 parts of sodium hydroxide (100%) in the form of an aqueous solution consisting of 40 wt. % of sodium hydroxide and 60 wt. % water. Heating was then initiated and the temperature of the reaction mass was raised over a period of about 2 hours to 425°F. which was maintained for about 1/4 hour. The grease was then cooled, while mixing, to 250°F. where 1 part of phenyl-alpha-naphthylamine was added as an oxidation inhibitor. After this, the grease was further cooled to 120°F. where it was homogenized in a Gaulin homogenizer thereby forming a uniform smooth structure.

EXAMPLE II

A grease was prepared in the same general manner as that of Example I except that 4 parts of 1,12-dodecane dicarboxylic acid was used in place of sebacic acid.

Comparison Grease A

This grease was prepared in the same general manner as Example I except that 4 parts of azelaic acid was used in place of sebacic acid.

The greases of Examples I and II, and Comparison Grease A were subjected to a number of standard tests and also a ball bearing temperature rise test. In this latter test, a 204 mm steel ball bearing is packed with 3.0 grams of the grease to be tested and the bearing is then operated at 10,000 rpm while the temperature of the grease in the bearing is continually measured by thermocouples placed on the outer bearing race.

The formulations of the above grease compositions and their physical properties are summarized in Table I which follows:

TABLE I

Examples

Formulation (% Wgt.)	I	II	Grease A
Glacial Acetic Acid	10.0	10.0	10.0
Iso-oleic Acid	15.0	15.0	15.0
Sebacic Acid	4.0	—	—
1,12-dodecanedioic acid	—	4.0	—
Azelaic Acid	—	—	4.0
Sodium Hydroxide	11.5	11.5	11.5
Phenyl-alpha-naphthylamine	1.0	1.0	1.0
Mineral Lubricating Oil, 55 SUS. at 210°F.	58.5	58.5	58.5
Properties			
Appearance	Excellent, Smooth grease	Excellent, Smooth Grease	Grainy
Dropping Point, °F.	500+	500+	500+
ASTM Penetration, 77°F./mm/10			
Unworked	290	290	290
Worked 60 strokes	310	310	310
Worked 10000 strokes	300	300	300
Roll Milled unworked	198	198	198
450°F. Beaker Test*	No phase change, slight softening	No phase change, slight softening	No phase change, slight softening
Lubrication Life,**10000 RPM			
250°F.	2000+	2000+	No further testing
300°F.	2000+	2000+	due to poor appearance
350°F.	500	450	of grease
Temperature Bearing Rise			
Room temp. °F. start	80	80	
15 minutes running	140	135	
1 hour running	90	95	
24 hours running	85	85	

*Consists of slow heating to 450°F. while slowly stirring and observing changes, if any, in the consistency of the grease.

**ABEC—NLGI Spindle Test.

As seen by the preceding table, greases of Examples I and II were excellent uniform soft greases saving good lubrication life, while the comparison Grease A gave a grainy gritty grease. This illustrates the criticality of the molecular weight of the dicarboxylic acid, since molecular weights below 190 are less suitable.

A series of comparisons between the greases of the invention and two closely related prior art sodium complex mixed salt grease sold for ball-bearing lubrication and hereinafter designated Grease B and Grease C was carried out.

Grease B consisted of mineral lubricating oil thickened with a sodium mixed-salt thickener prepared by coneutralizing with sodium hydroxide a mixture of stearic acid and acetic acid, followed by heating to 410°F. until dehydrated and of satisfactory soap dispersion. The grease is then cooled, and an oxidation inhibitor is added, followed by further cooling to 110°F. where the grease is Morehouse milled and then packaged.

Grease C was a grease prepared by alkali-fusion of rapeseed oil.

In this process, rapeseed oil is heated in mineral oil with sodium hydroxide to hydrogen evolving temperatures to form mixed sodium salts of high and low molecular weight carboxylic acids resulting from the alkali fusion.

Greases B and C are both premium ball-bearing greases and the latter has been a leader in its field for about 20 years. Greases B and C are each currently sold in hundreds of thousand pounds per year.

The lubrication lives of greases of Example I and Greases B and C in the ABEC-NLGI spindle test carried out using a 204 mm antifriction ball-bearing operating at 10,000 revolutions per minute at different temperatures are summarized in Table II, which follows:

TABLE II
Lubrication Life, ABEC-NLGI Spindle Test

Grease	Life in Hours		
	250°F.	300°F.	350°F.
Grease B	1800	350	50
Grease C	2000	300	50
Grease of Example I	2000+	2000+	500

As seen by Table II, the grease of Example I, was superior to the two commercial greases, particularly at the higher temperatures. The significance of this difference in actual practice is that electric motors and other high temperature appliances of advanced design can now be operated and satisfactorily lubricated for considerably longer periods of time and at higher temperatures than could be obtained by these prior premium bearing greases.

A pressure viscosity test was carried out on the greases of Examples I and II compared with the prior art complex Grease C, described above. This test was carried out by forcing the grease at the rate of 3 cubic cms. per minute through a capillary of 0.002" at varying temperatures while measuring the pressure in terms of pounds per sq. inch required to maintain the 3 cc/min rate of flow. This test provides an indication of viscosity of the grease as it behaves under pressure at varying temperatures. The results of these tests are plotted on the graph of the accompanying drawing which shows that the greases of Examples I and II consistently and slowly declined in their apparent viscosity upon increasing temperatures. On the other hand, the prior art grease (Grease C) actually began to thicken or increase in viscosity at temperatures of below 300°F., after which it again began to decline in viscosity. This latter phenomenon had been somewhat of a drawback in the marketing of this prior complex grease insofar as this indicates a phase change in the soap thickener system, changing from a smooth uniform dispersion capable of excellent lubrication, to a rubbery fibrous unhomogeneous dispersion which is no longer capable of good lubrication.

As indicated above, the greases of the invention can be further improved by incorporating finely divided phosphate into the grease. This will be illustrated by the following examples:

EXAMPLE III

Part A—10 parts of Nalcamine G-39-M and 17.8 parts of mineral lubricating oil

were mixed together, and 2.2 parts of phytic acid (100%) was then added in the form of a 70% aqueous solution. This resulted in forming the Nalcamine phytate which thickened the oil to a grease consistency. 70 parts of hydrated trisodium ortho phosphate ($\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$) was then added in the form of a 40 wt. % aqueous solution. The entire mixture was then heated to boiling until about 50 wt. % of the free water present was removed by evaporation. Upon cooling, the composition was a very stable gel having a total water content of 50 wt. %, based on the total weight of said gel.

Part B—A grease was prepared as follows:

59.5 parts of mineral lubricating oil of 55 SUS at 210°F., 15 parts of the isooleic acid (same as in Examples I and II), and 4 parts of dibasic alkyl aromatic acid obtained from a catalytic cycle stock extract was charged to a fire-heated grease kettle and intimately mixed. To this mixture was added 10 parts of glacial acetic acid, followed immediately by the addition of 10.5 parts of sodium hydroxide in the form of an aqueous solution consisting of 40 wt. % sodium hydroxide dissolved in 60 wt. % water. Heating was initiated and the temperature of the reaction mixture was raised to 440°F., which temperature was maintained for about 15 minutes. The grease was then cooled to 250°F., where 1 part of phenyl-alpha-naphthylamine was added as an oxidation inhibitor, after which the grease was further cooled to 100°F. A portion of the grease was then removed and homogenized in a Gaulin homogenizer operating at 1500 psi.

Part C—The balance of the grease remaining in the grease kettle was reheated to 400°F. where 4 parts of the colloidal dispersion of sodium phosphate in mineral oil stabilized with the reaction product of imidazoline and phytic acid (product of Part A) was then added. The grease was again cooled while agitating to 100°F. where it was homogenized in a Gaulin homogenizer operating at 1500 psi.

The alkyl aromatic dicarboxylic acid used above was a mixture of acids having molecular weights of 450 to 550. This acid had a saponification number of 200 mg. KOH/gram. It was derived from an aromatic extract by treatment with sodium, then CO_2 , followed by hydrolysis. The extract was obtained by extraction of a catalytic cycle stock. This stock consisted of about 17 wt. % 3-ring aromatics, and about 63 wt. % 4-ring aromatics, the remainder being mainly naphthenes with small amounts of thiophenes, paraffins, etc. The acid was prepared from the stock as follows:

One-half mole equivalent of catalytic cycle extract was dissolved in 350 ml. of tetrahydrofuran (THF) and added dropwise to a stirred mixture of 1 gram atom of sodium metal chips in 150 ml. THF. During the 3 hours addition time, the reaction mixture became reddish, then finally black, and the temperature rose from about 26° to 36°F. After the addition was completed, the reaction mixture was heated to reflux (about 68°C.) and stirred at reflux temperature for an additional 3.75 hours. Nearly all of the sodium metal had reacted, indicating that the disodio adduct of the reactive polynuclear aromatic hydrocarbons in the feed had formed. The disodio adduct was then poured in an inert atmosphere onto several pounds of powdered solid carbon dioxide, the resultant slurry stirred several times, and the mixture then allowed to stand until the excess carbon dioxide evaporated. After the mixture had warmed to room temperature, 25 ml. of methanol was added with stirring to destroy any excess sodium metal. About 2000 ml. of water was added and the mixture allowed to stand. The organic layer (containing unreactive components of the aromatic extract feed) was separated from the water layer, and the water layer washed with successive portions of pentane. Dilute hydrochloric acid (90 ml. concentrated hydrochloric acid in 250 ml. water) was added to the aqueous layer. The acidified mixture was extracted with successive portions of diethyl ether to remove the carboxylic acid product. Evaporation of the ether yielded a syrupy mixture of the polynuclear aromatic acids used above.

EXAMPLES IV TO VI

A series of greases were prepared as follows:

Mineral lubricating oil, isooleic acid, and sebacic acid were mixed in a grease kettle. Glacial acetic acid was then added to the mixture followed immediately by the addition of sodium hydroxide in the form of an aqueous solution containing 40 wt. % sodium hydroxide. The composition was then heated to about 300°F. where trisodium phosphate was added in the form of an aqueous solution containing 50 wt. % of $\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$. Heating was then continued to about 450°F. to dehydrate the grease which was then cooled while stirring to 250°C. where phenyl-alpha-naphthylamine was added as an oxidation inhibitor. The product was then allowed to cool to about 100°F. where it was passed through a Gaulin homogenizer operating at about 1500 psi.

The compositions and some of the various properties of the greases of Examples III to VI are summarized in Table III which follows:

TABLE III

Formulation (Wgt. %)	Examples				
	III-B	III-C	IV	V	VI
Glacial Acetic Acid	10.0	9.6	6.82	10.0	10.0
Isooleic Acid	15.0	14.4	10.23	15.0	15.0
Alkyl Aromatic Dicarboxylic Acid	4.0	3.8	—	—	—
Sebacic Acid	—	—	2.73	4.0	4.0
Sodium Hydroxide	10.5	10.0	7.84	11.5	11.5
Sodium Phosphate	—	4.0**	2.73	3.0	4.0
Phenyl α -Naphthylamine	1.0	1.0	0.68	1.0	1.0
Mineral Oil	59.5	57.2	68.97	55.5	54.5
Mole eq. ratio-Acetic/dicarb. acid	10/1	10/1	4.2/1	4.2/1	4.2/1
Mole eq. ratio-Isooleic/dicarb. acid	3.3/1	3.3/10	1.2/1	1.3/1	1.3/1
Properties:					
Appearance	Excellent smooth grease	Excellent smooth grease	Excellent	Excellent	Excellent
Dropping Point, °F.	500	500	475	500	500
ASTM Penetrations, 77°F., mm./10	204	250	248	201	212
Unworked	250	282	255	216	252
Worked 60 strokes	282	292	312	272	282
Worked 10000 strokes					
Lubrication Life*, 10000 rpm. in hours	2000+	2000+	—	2000+	2000+
250°F.	728	2000+	1300	2000+	2000+
300°F.	275	344	—	445	435
350°F.					

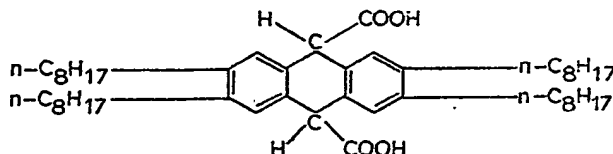
*ABEC—NLGI Spindle Test

**Colloidal dispersion

As seen by a comparison of the composition of Example III-C with III-B the addition of the trisodium phosphate materially increased the lubrication life at the 300°F. and 350°F. level. Also, the composition of Example IV shows the longer lubrication life obtained at the 300°F. level, while the compositions of Examples 5 and 6 show that upon increasing the amount of trisodium phosphate, even longer high temperature lubrication lives were obtained.

EXAMPLE VII

Example III, Parts B and C are repeated, except that 4 parts of dibasic alkyl aromatic acid of the structure



is used in place of the aromatic acid of Example III, and the amount of sodium hydroxide used is such as to give a neutral product.

While the preceding Examples have been directed primarily to greases suitable for bearing lubrication, other lubricating uses of the compositions of the invention are contemplated.

According to a further specific embodiment of the present invention, it has been found that by using lithium and predominantly saturated high molecular weight acid, the resultant grease is water-insoluble in both cold and boiling water. In view of this water insolubility, the grease can be employed in marine service and other services where these bearings, or the grease itself, may be subjected to high humidity, water vapor or other sources of moisture. This water insolubility, however, will require the use of a ferrous metal rust inhibitor for most applications. We have also found that certain mole ratios of the various acid components are particularly preferred for making lithium greases, that by using these mole ratios, azelaic acid as the dicarboxylic acid component can be used, and that some calcium salt can be also used to advantage in the grease. The use of azelaic acid permits the formation of a more economical grease due to its relatively low cost as compared to other suitable dicarboxylic acids. Using calcium in place of part of the lithium permits further economy in manufacture due to the lower cost of the calcium base. Also by using calcium, a larger amount of unsaturated fatty acid can be used, without destroying the water-insolubility of the grease. Thus, an all-lithium grease with all-unsaturated fatty acid will become water-soluble, particularly in hot water. An all-calcium grease using the acids and relative ratio of acids of the present invention would have poor structural stability without the presence of water or other stabilizing agents. However, the presence of water is undesirable since it prevents the effective use of the grease at high temperatures due to loss of the water at high temperatures, while stabilizing agents would increase the cost of the lubricant, and in some cases undesirably change its properties.

The mixed-salt thickener systems of this embodiment of the invention are best made to contain metal salt of 0.5 to 3.0, preferably 1 to 2 molar hydrogen equivalents of low molecular weight C_2 to C_4 fatty acid per molar hydrogen equivalent of dicarboxylic acid. These systems will also preferably contain metal salt of 0.5 to 3.0, preferably 1 to 2 molar hydrogen equivalents of C_{12} to C_{24} high molecular weight fatty acid per molar hydrogen equivalent of said dicarboxylic acid. Greases can be thus prepared having a total content of said metal salts of 5.0 to 49.0 weight percent, preferably 15 to 35 weight percent, based on the total weight of the grease. The grease, in turn, can be diluted with additional oil to form fluid or semi-fluid compositions containing 0.1 to 5.0% of the mixed salt.

The metal can be all lithium, or a mixture of lithium and calcium in a ratio of 1 to 4 parts by weight of lithium per part by weight of calcium.

EXAMPLE VIII

68.3 parts of mineral lubricating oil of 60 SUS at 210°F., 15 parts of Hydrofol Acids 51 as the higher fatty acid, and 3 parts of azelaic acid were added to a fire heated grease kettle and mixed while stirring to 125°F. 3 parts of glacial acetic acid was rapidly added to the kettle contents, followed by the addition of 5.7 parts of lithium hydroxide monohydrate added in the form of an aqueous solution containing

10 wt. % of the lithium monohydrate. The kettle contents were mixed and heated to 425°F. to dehydrate the composition. The 425°F. temperature was held for about 15 minutes. The heat was turned off and the kettle cooled by passing water through the kettle jacket. In about 60 minutes, the kettle contents was cooled to about 250°F., while continuously stirring. Then 1 part of phenyl-alpha-naphthylamine was added as an oxidation inhibitor, after which the grease was cooled to 120°F. At this point, 2 parts of finely divided sodium nitrite (1.0 to 35 microns) was added in a 50/50 mixture of sodium nitrite and mineral lubricating oil of 50 SUS viscosity at 210°F. After the addition of the sodium nitrite, the product was homogenized by passage through a Morehouse mill to form the finished grease.

Hydrofol Acid 51 is a commercial acid having an average chain length of about 18 carbon atoms and similar to stearic acid in degree of unsaturation, having a Wijs iodine number of about 3 maximum. Hydrofol Acid 51 is prepared by hydrogenating fish oil acid (menhadden).

EXAMPLE IX

A grease was prepared following the same general procedure of Example VIII except that the higher fatty acid consisted of a mixture of (a) Hydrofol Acid 51 and (b) tallow fatty acid having a saponification number of 203 and a Wijs iodine number of 55. Also slightly different amounts of mineral oil and lithium hydroxide were used (See Table IV).

EXAMPLE X

A grease was prepared in the general manner of Example VIII except that a portion of the lithium hydroxide monohydrate was replaced by hydrated lime, and slightly different proportions of reactants were used (See Table IV).

The compositions of Examples VIII to X and their main properties are compared with a prior art premium ball bearing grease made from lithium hydroxy stearate in the following table:

TABLE IV

Composition (Wt. %)	Examples			Lithium Hydroxy Stearate Grease
	VIII	IX	X	
Glacial Acetic Acid	3.0	3.0	3.0	—
Hydrofol Acid 51	15.0	10.0	15.0	11.0
Tallow Fatty Acids	—	5.0	—	—
Azelaic Acid	3.0	3.0	3.0	—
Lithium Hydroxide Monohydrate	5.7	1.0	4.1	1.8
Hydrated Lime	—	—	2.0	—
Phenyl α -Naphthylamine	1.0	1.0	1.0	1.0
NaNO ₃	2.0	2.0	2.0	2.0
Mineral lube oil 60 SUS at 210 °F.	68.3	67.9	67.9	82.2
Mineral lube oil 50 SUS at 210 °F.	2.0	2.0	2.0	2.0
Mole H. eq. ratio, acetic/azelaic	1.57	1.57	1.57	—
Mole H. eq. ratio, higher fatty acid/azelaic	1.66	1.66	1.66	—
Properties:				
Appearance	Excellent	Excellent	Excellent	Excellent
Dropping Point, °F.	450+	450+	450+	355
ASTM Penetration, 77 °F., mm/10				
Unworked	205	220	240	260
Worked 60 strokes	210	225	245	265
Worked 10,000 Strokes	225	230	285	280
400 °F. Beaker Test	Other than slight softening, no phase change			Phase change at 325 °F. Melts at 230 °F.
Solubility in Boiling Water	Insoluble	Insoluble	Insoluble	Insoluble
Norma Hoffman Oxidation Test, Hrs. to 5 psi. Drop	6	6	5	25
Accelerated Wheel Bearing Test, 220 °F., 1 Hour,				
45 ° Angle	Pass	Pass	Pass	Pass
Slump	None	None	None	None

TABLE IV (Continued)

Composition (Wt. %)	Examples			Lithium Hydroxy Stearate Grease
	VIII	IX	X	
Leakage Grams	0.6	0.2	1.0	5.0
Lubrication Life,* Hours				
10,000 RPM 250°F.**	2000+	2000+	2000+	1120
300°F.	400	625	740	120
Ball Bearing Temperature Rise Test at 10,000 rpm., °F.				
Initial Rise	10	15	15	65
Steady State Condition, °F.	80	80	80	175
Rust Test CRC L-41	Pass	Pass	Pass	Pass

*ABEC—NLGI Spindle Test.

**Test discontinued after 2,000 hours.

The 400°F. Beaker Test was carried out by slowly heating the grease in a beaker while stirring to determine if there was any change in structure.

The Wheel Bearing Test was carried out as described in ASTM Designation D-1263-53T with the exception that the test was run at a 45° angle to accelerate any leakage.

The Ball Bearing Temperature Rise Test was carried out as follows: A 204 mm. steel ball bearing was packed with 3.0 grams of the grease to be tested and the bearing was then operated at 10,000 rpm while the temperature of the grease in the bearing was continually measured by thermocouples placed on the outer bearing race.

The CRC L-41 test was carried out by coating chemically clean Timken (R.T.M.) bearings (cup and bearing) with a thin coating of the grease and subjecting the bearing to turning at 1600 rpm under a load to spread the grease in a thin layer. The cup and bearing assembly were then dipped in water and stored for 14 days in a closed glass jar containing a small amount of water so as to maintain a humid atmosphere. After 14 days the bearing was then examined for rust.

As seen by the data of Table IV the greases of the invention, represented by Examples VIII to X had dropping points in excess of 450°F. These are extremely high dropping points for lithium grease since the lithium hydroxystearate grease, which is a premium ball bearing lithium grease, has a dropping point of 355°F. In the 400° Beaker Test, there was no change in the inventive greases of Examples VIII to X other than a slight softening, whereas the comparison grease melted at 350°F. The inventive lithium greases were all insoluble in boiling water and had improved wheel bearing test characteristics as noted by their lack of slump and their low leakage. In addition, the

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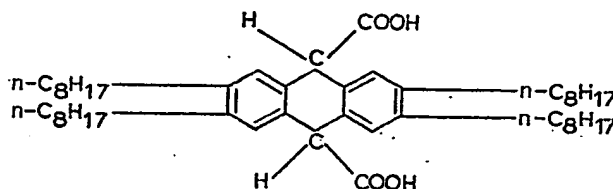
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greases of the invention had lubrication lives at 250°F. in excess of 2,000 hours as compared to only 1120 hours for the lithium hydroxystearate grease. At the 300°F. test level, the lithium hydroxystearate grease lasted only 120 hours, while the greases of the Examples ranged from 400 to as much as 740 hours of operation before failing. The improvement represented by the inventive greases is even more strikingly demonstrated by their operation in a ball bearing. Here it is seen that upon operating the bearing, the greases of Examples VIII to X gave an initial temperature rise of only 10 to 15°F. above the ambient temperature of 75°F., after which the temperature fell to 80°F. after which the bearing then operated continuously at 80°F. On the other hand, the prior art lithium hydroxystearate grease, which was non-channelling, gave an initial bearing rise of 65°F. and then began to further increase in temperature until it settled at a temperature of 175°F., although the ambient temperature was 75°F.

Example VIII thus illustrates an all-lithium grease of the invention prepared from a saturated commercial fatty acid. Example IX illustrates that good greases can be prepared using predominantly (i.e. more than 50%) saturated high molecular weight fatty acid. While Example X illustrates the replacement of part of the lithium with calcium.

EXAMPLE XI

Example VIII is repeated except that 3 parts of dibasic alkyl aromatic acid of the structure:



is used in place of the azelaic acid of Example I, and the amount of lithium hydroxide monohydrate used is such as to give a neutral product.

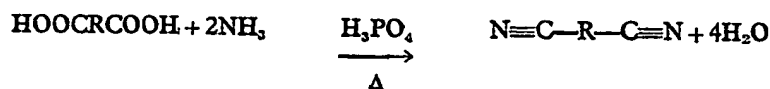
The lubricating composition according to the invention may also contain from 0.1 to 10.0 wt.% of a C_{10} to C_{32} aliphatic dinitrile as lubricant additive. These dinitriles are very useful as plasticizers for greases, and for preparing greases which can change from soft greases to hard greases during shearing use, i.e. greases which shear harden. This ability to shear harden is of particular importance in the lubrication of anti-friction ball bearings. In ball bearing lubrication, a non-hardening type grease tends to churn in the rotating bearing, imparting resistance to the rotation of the bearing, thereby increasing friction and generating heat. On the other hand, when using a shear-hardening grease, the rotating ball bearings form a channel through the grease so that the grease does not impede the balls or bearing movement, thereby giving lower torque requirements, less friction and a cool running bearing. By the reduction of friction, considerably less power is required, which is particularly noticeable in long, bearing-supported gear trains. For the preceding reasons, channelling-type grease is preferred for the lubrication of anti-friction bearings for lubricated-for-life electric motors. However, during inspection of new motors, a channelling-type grease may permit loud whistling, and other bearing noises. These noises are very undesirable because it is therefore difficult to tell if the bearing is actually defective, or if the noise is normal. On the other hand, a non-channelling type grease, by churning in an operating bearing, dampens this normal bearing noise (which is usually caused by separator-flutter) so that if the bearing is still noisy, it is probably defective. One aspect of this invention involves therefore the inclusion of these dinitrile in the grease composition which allows short-term initial churning of the grease in bearings to prevent bearing noise during inspection of the bearing and motor, after which time the grease gradually becomes a channelling grease.

The dinitrile which can be included in the compositions of the invention can be represented by the general formula:



wherein R is an aliphatic hydrocarbon radical, straight chain or branched chain, saturated or unsaturated, containing 8 to 30, preferably 8 to 20, carbon atoms. Specific examples of such dinitriles are dodecanedioic dinitrile (also known as 1,10-dicyanodecane), sebaconitrile (from sebacic acid), and brassylonitrile (from brassylic acid).

The dinitrile can be prepared by reacting a dicarboxylic acid with ammonia in the presence of phosphoric acid while removing water of dehydration. This reaction takes place as follows:



5 After completion of the reaction, the dinitrile is recovered and simultaneously purified by distilling dinitrile from the reaction mixture. Or, the crude reaction mixture which contains the desired dinitrile together with varying amounts of the corresponding α,ω aliphatic acid-nitrile, amide-nitrile, diamide, and diacid can be used. 5

10 These dinitriles will hydrolyze with water readily at elevated temperatures. Usually they are hydrolyzed by base and then split to give ammonia and the salt of the acid. In certain embodiments of the present invention, this hydrolyzation is taken advantage of to form metal salts of dicarboxylic acid or to form metal salt of monocarboxylic acid-mononitrile, i.e. the half hydrolyzed aliphatic dinitrile which can be presented by the formula: 10



In any event, the dicarboxylic acid or the monocarboxylic acid, or metal salts thereof, when formed from the dinitrile, are considered as derivatives of the dinitrile for purposes of this invention.

20 The dinitrile is dispersed in the composition according to the invention in amounts of 0.1 to 10.0 wt.%, e.g. 0.5 to 5 wt.%, based on the total weight of the composition. 20

EXAMPLE XII

25 *Part A*—Preparation of dodecanedioic dinitrile (also called 1,10-dicyanododecane). 230 grams of dodecanedioic acid and 23 g. of concentrated ortho phosphoric acid (85 wt.% ortho phosphoric acid and 15 wt.% water) were added to a 2-liter, four-neck flask. The flask was equipped with a stirrer, thermowell, ammonia inlet tube, and a Dean-Stark trap and condenser to remove the water of dehydration. The flask and its contents were heated to 300°C. with a constant supply of ammonia entering the bottom of the flask at a rate of approximately 0.5g./min. The water of dehydration was removed continuously while the temperature was maintained at 300°C. for eight hours. After eight hours, the flask was cooled to room temperature. The reaction mixture was then distilled under 0.8 mm. Hg. pressure to give 160 g. of dodecanedioic dinitrile (85% yield) as a residue having a boiling point of 148°C. at 0.8 mm. Hg. pressure. 25

30 *Part B*—A grease composition was prepared utilizing the dodecanedioic dinitrile of Part A as prepared above. Specifically, 10 parts of Hydrofol Acids 51 and 60 parts of a mineral lubricating oil of 55 SUS viscosity at 210°F. were added to a fire-heated grease kettle and mixed while heating to 125°F. Hydrofol acid 51 is a commercial acid obtained by hydrogenating fish oil, and has an average chain length corresponding to stearic acid. 6 parts of sodium hydroxide in the form of a 40 wt.% aqueous solution (i.e. 40 wt.% sodium hydroxide and 60 wt.% water) were added to the kettle. Immediately after adding the sodium hydroxide solution, a blend consisting of 4 parts of glacial acetic acid and 10 parts of the dinitrile of Part A were then added to the kettle. The temperature of the mixture in the kettle was then raised by heating and the following heating schedule was then observed: 35

40 40

Heating Schedule After Addition of All Reactants

Minutes	°F.	Remarks
0	260	Water coming off
15	390	Dry, closed kettle
20	480	—
30	550	Shut off heat
35	440	—
40	390	—
70	200	—
75	175	Stopped agitation

1 part of phenyl α -naphthylamine was added as an oxidation inhibitor when the grease had cooled to 250°F.

5 *Part C*—A portion of the grease prepared above in Part B was homogenized while at a temperature of about 100°F. by passage through a Morehouse mill operating at a 0.003" opening to thereby give a relatively low rate of shear. 5

Part D—A portion of the Morehouse milled grease of Part C was roll milled while at a temperature of about 100°F. using a roll opening space of 0.001" to thereby give a relatively high rate of shear and form the final grease product of Example I.

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EXAMPLE XIII

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A sample of the final grease product of Example XII Part D was further homogenized in a Manton-Gaulin homogenizer operating at 10,000 psi. pressure to result in a shear of about 500,000 reciprocal seconds. After Gaulin homogenizing, the grease was then further diluted with an equal amount of mineral lubricating oil of 55 SUS viscosity at 210°F. The compositions of the greases of Examples XII and XIII are summarized in the following table along with their more pertinent properties.

15

TABLE V

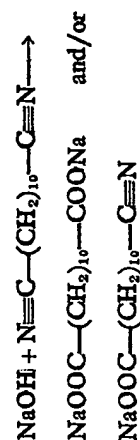
Greases

Composition (Wt. %)	Example XII	Example XIII
Dodecanedioic dinitrile	10.0	5.0
Hydrofol Acids 51	10.0	5.0
Glacial Acetic Acid	4.0	2.0
Sodium Hydroxide	6.0	3.0
Phenyl α -naphthylamine	1.0	0.5
Mineral Lubricating Oil 55 SUS. at 210°F.	69.0	84.5
Properties:	Part B Unmilled	Part C Morehouse Milled
Appearance	Smooth	Smooth & glossy
Dropping Point, °F.	500+	500+
ASTM Penetration 77°F., mm/10	330	210
Unworked	320	215
Worked 60 Strokes	315	225
Worked 10,000 Strokes	Pass	Pass
Wheel Bearing Test, 220°F.	20% Leakage	10% Leakage
Water Washing—Cold Water*	2.0	—
Norma Hoffmann Oxidation, Hours to 5 psi. drop	2000+	—
Lubrication Life,** Hours	2000+	—
250°F.—10,000 RPM	—	2000+
300°F.—10,000 RPM	—	—

*ASTM D 1264—53T

**ABEC NLGI Spindle Test

In the greases of Examples XII and XIII, a portion of the dodecane dinitrile probably remained unchanged and served as a plasticizer and dispersant, while another portion of the dodecane dinitrile was probably converted to sodium salt as indicated by the following reaction:



It appears that any base above the amount necessary to neutralize the acetic and Hydrofol acids is used up in reaction with the dinitrile. Parts B, C, and D illustrate the hardening of the grease under shear resulting from the milling. This ability to harden so drastically under shear is believed to be due to the presence of sodium salt of dicarboxylic acid.

To further demonstrate the outstanding utility of the greases of the invention for bearing lubrication, a bearing temperature rise test was carried out as follows:

A 204 seven ball bearing was packed with 3.0 grams of the grease of Example XII, Part B and the bearing was then operated at 10,000 rpm while the temperature of the grease in the bearing was continuously measured by thermocouples placed on the outer bearing race.

In comparison, a commercial sodium salt bearing grease was also run in the above bearing test. This commercial grease consisted of mineral lubricating oil thickened with a sodium mixed-salt thickener prepared by coneutralizing with sodium hydroxide a mixture of stearic acid and acetic acid, followed by heating until dehydrated and of satisfactory soap dispersion. This commercial grease contained a small amount of anti-oxidant.

The results of the bearing test are summarized in Table VI which follows:

TABLE VI
Bearing Temperature Rise—10,000 RPM

	Example XII Part B	Comparison Typical Sodium Soap Grease
Ambient Temperature	70°F.	70°F.
Start	70°F.	70°F.
2 Min. Running	100°F.	150°F.
5 Min. Running	130°F.	185°F.
10 Min. Running	85°F.	185°F.
24 Hours Run	85°F.	187°F.
Power Requirement	Low	High

As seen by Table VI above, the grease prepared from the dodecanedioic dinitrile showed an initial temperature rise up to 130°F. during the first five minutes of operation, but then quickly fell off to 85°F. This indicates that during the first few minutes of operation, some slight churning of the grease occurred, but the grease quickly formed a channel for the rotating balls with a resultant drop in temperature. On the other hand, the commercial bearing grease rose to 185°—187°F. and maintained this temperature, thus indicating continuous churning. As a result of this churning more power was required to operate the bearing running on the commercial grease than was required to operate the grease of the invention. This increased power requirement is of course wasted, since it performs no useful work.

EXAMPLE XIV

A lubricating grease composition was prepared as follows:

10 parts of Hydrofol Acids 51, 5 parts of dodecanedioic acid and 69 parts of mineral lubricating oil of 55 SUS. viscosity at 210°F., were added to a grease kettle and heated to 150°F. 4 parts of glacial acetic acid was next added, followed immediately by the addition of 6 parts of sodium hydroxide which were added in the form of an aqueous solution containing 40 wt.% sodium hydroxide and 60 wt.% of water. The reaction mixture was then heated at 450°F. for about 2 hours. Heating was discontinued and the grease was allowed to cool to 250°F. where 1 part of phenyl-alpha-naphthylamine was added as an oxidation inhibitor, after which the grease was further cooled to 150°F. 5 parts of dodecanedioic dinitrile was then added and the grease was homogenized in a Charlotte mill and packaged.

Comparison Grease—(No dinitrile in formulation)

- 5 A grease was prepared by adding 10 parts of dodecanedioic acid, 16 parts of Hydrofol Acids 51 and 66.5 parts of mineral lubricating oil of 55 SUS. viscosity at 210°F. to a fire-heated grease kettle and warmed to 150°F. while stirring. 4 parts of glacial acetic acid was then added, followed immediately by the addition of 8.5 parts of sodium hydroxide in the form of a 40% solution of sodium hydroxide and 60 wt.% water. Heating was continued and the temperature of the composition raised to 450°F. which was held for about two hours. Heating was then discontinued and the grease was allowed to cool to 250°F., where 1 wt. % of phenyl-alpha-naphthylamine was added, after which the grease was further cooled to 100°F. The rather rough textured grease product was then Morehouse milled. After milling, the grease still retained a somewhat rough texture.
- 10
- 5
- 10

EXAMPLE XV

(Dinitrile in formulation)

- 15 A grease was prepared in the same general manner as that of the comparison grease just described, except that 2 parts of dodecanedioic dinitrile was used in place of 2 parts of dodecanedioic acid.
- 15

The compositions of Examples XIV and XV, the comparison grease, and their properties are summarized in Table VII which follows:

TABLE VII

Formulation	Examples	
	XIV	XV
Dodecanedioic Acid	5.0	10.0
Dodecanedioic dinitrile	5.0	—
Hydrofol Acids 51	10.0	10.0
Glacial Acetic Acid	4.0	4.0
Sodium hydroxide	6.0	8.5
Phenyl α -Naphthylamine	1.0	1.0
Mineral Lubricating Oil of 55 SUS. at 210°F.	69.0	66.5
Properties:		
Appearance	Excellent, smooth grease	Rough
Dropping Point, °F.	500+	500+
ASTM Penetration 77°F. mm/10		
Unworked	285	210
Worked 60 strokes	300	250
Worked 10,000 + strokes	310	255
Wheel Bearing Test, 220°F.	—	Pass, No Slump
Water Washing Test, Loss %	—	Pass, No Leakage
Norma Hoffman Oxidation	—	20
Hours to a 5 psi drop in O ₂ Press	175	200
Lubrication Life, 10,000 rpm, 250°F.	2000+	2000+
Bearing Temperature Rise, °F., 10,000 rpm.		
Start	75	70
5 Minutes	—	130
10 Minutes	—	85
30 Minutes	160	—
2 Hours	160	—
24 Hours	145	85
6 Days	90	—

As seen, the dinitrile of Example XIV very slowly reacted to form salt as indicated by the slow change from a non-channelling grease to a channelling-type grease at the end of 6 days operation in the 204 bearing. Apparently, the dinitrile hydrolyzed and reacted with the excess sodium hydroxide to make primarily the disodium salt of dodecanedioic acid. Example XV and the Comparison were both channelling greases as seen by the low temperature of the bearing after 10 minutes operation. However, the Comparison, which contained no dinitrile, had a rough coarse appearance, while the grease of Example XV containing the dinitrile was smooth and homogeneous, thus illustrating the plasticizing effect of the dinitrile. Also, Example XIV illustrates that when the dinitrile is added at low temperatures (e.g. at 150°F. in Example XIV) to a grease, the dinitrile is not quickly converted to the metal salt, but rather changes very gradually to said salt when used in a bearing. On the other hand, when the dinitrile is heated to a high temperature (as in Example XII) with excess metal base present, the dinitrile is quickly converted to its metal carboxylic acid salt derivative. It is thus seen, that by regulating: (1) the amount of metal base present, the extent to which the dinitrile is converted to salt can be controlled and (2) by determining the temperature at which the dinitrile is added to the grease reaction mixture the rate with which the grease shear hardens can be controlled. Thus, depending on the end use, greases can now be designed which can shear harden to a degree of hardness in a desired time. Thus, the dinitrile offers the grease-maker a new and valuable tool in making grease. In addition, the dinitrile acts as an anti-oxidant. Thus, the grease of Example XV, without the 1 part of phenyl-alpha-naphthylamine, ran over 1,000 hours in the 204 bearing test, while similar sodium greases without either the nitrile or an oxidation inhibitor usually fail in about 300 hours in said bearing test.

WHAT WE CLAIM IS:—

1. A lubricating grease composition comprising a major amount of lubricating oil and a minor amount of a mixed salt combination of alkali metal salts of a) C₂ to C₄ fatty acid, b) C₆ to C₁₆ aliphatic dicarboxylic acid or alkyl polynuclear aryl dicarboxylic acid and c) C₁₂ to C₂₄ fatty acid, in a molar hydrogen equivalent ratio of 1 to 10 molar hydrogen equivalent proportions of the C₂ to C₄ fatty acid per molar hydrogen equivalent of the dicarboxylic acid, and 1 to 4 molar hydrogen equivalents of the C₁₂ to C₂₄ fatty acid per molar hydrogen equivalent of said dicarboxylic acid.

2. The composition according to Claim 1 wherein said C₂ to C₄ fatty acid is acetic acid.

3. The composition according to Claim 1 or Claim 2 wherein said aliphatic dicarboxylic acid is a C₁₀ to C₁₂ acid.

4. The composition according to Claim 1 or Claim 2 wherein said alkyl polynuclear aryl dicarboxylic acid has a total of 1 to 6 alkyl groups of 1 to 8 carbon atoms each and wherein the number of rings is 3 or 4.

5. A lubricating composition as claimed in any of the preceding claims wherein the mixed salt comprises 3 to 6 molar hydrogen equivalent proportions of the C₂ to C₄ fatty acid, 1 to 3 molar hydrogen equivalent proportions of the C₁₂ to C₂₄ fatty acid and 1 molar hydrogen equivalent of the dicarboxylic acid.

6. The composition according to Claims 1 to 5 wherein said alkali metal is lithium or sodium.

7. The composition according to claim 4, wherein said alkyl polynuclear dicarboxylic acid is a mixture of acids prepared from an aromatic extract derived by extraction of catalytic cracking cycle stock as hereinbefore described.

8. The composition according to claims 1—7 which also contains 0.1 to 6.0 wt. % of alkali metal phosphate.

9. A high temperature lubricating grease composition suitable for ball-bearing lubrication comprising a major amount of mineral lubricating oil, and 5 to 49 wt. % of a sodium mixed salt thickener system of acetic acid, C₆ to C₁₆ aliphatic saturated dicarboxylic acid and C₁₂ to C₂₄ fatty acid in a mole hydrogen equivalent ratio of 3 to 6 mole equivalent proportions of said acetic acid per mole equivalent of said dicarboxylic acid, and 1 to 4 mole equivalents of said C₁₂—₂₄ fatty acid per molar equivalent of said dicarboxylic acid.

10. A grease composition according to claim 9, wherein said dicarboxylic acid is sebacic acid.

11. A grease composition according to claim 9, wherein said dicarboxylic acid is 1,12 dodecanedioic acid.

12. A grease composition according to claim 9 also containing 1 to 6 wt. % trisodium orthophosphate.

13. A grease composition according to Claims 1 to 12 wherein said metal is lithium and the composition also contains calcium salts of said acids.

14. A grease composition according to Claim 13 wherein the lithium-calcium component consists of 1 to 4 parts of lithium per part of calcium.

5 15. A lubricating grease composition according to Claims 1 to 14 which also contains 0.1 to 10.0 wt. % of a C₁₀ to C₂₂ aliphatic dinitrile. 5

16. A grease composition according to Claim 15 wherein the aliphatic dinitrile is of the general formula:



10

wherein n is an integer of 8 to 30. 10

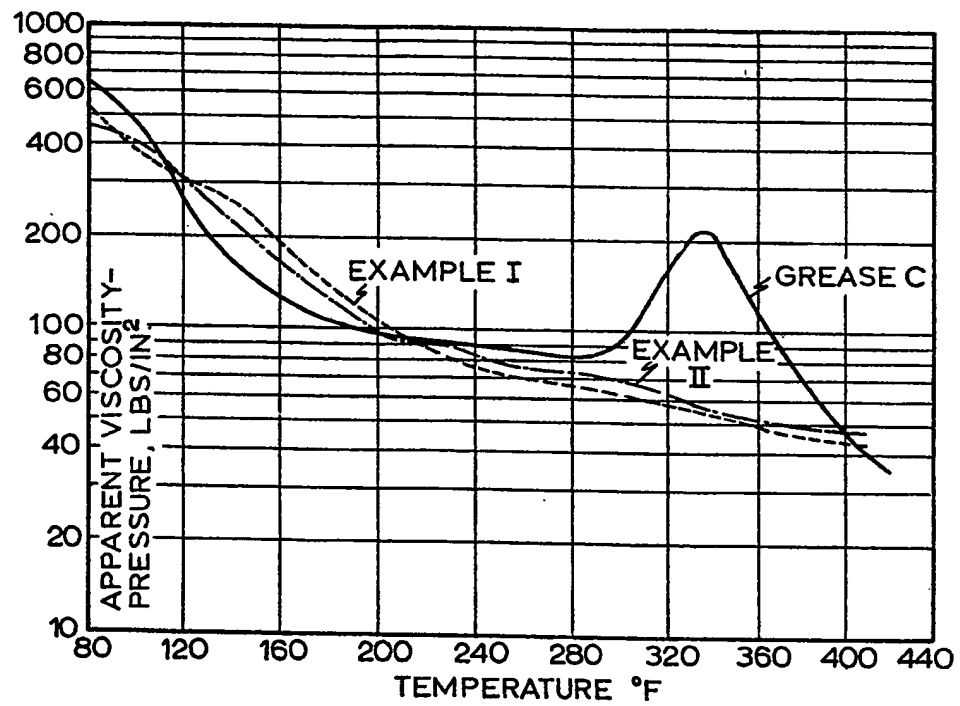
17. A grease composition according to Claims 15 or 16 wherein said dinitrile is dodecanedioic dinitrile.

15 18. A grease composition according to Claims 15 to 17 which contains unreacted sodium hydroxide in an amount sufficient to form sodium salt of a carboxylic acid derivative of said dinitrile upon hydrolysis of said dinitrile. 15

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- ☐ **FADED TEXT OR DRAWING**
- ☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☒ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

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